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Technical Report  
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CORROSION INHIBITION BY ORGANIC AMINES  
by

Norman Hackerman and Helmut Kaesche

April 16, 1957

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Department of Chemistry  
The University of Texas

Austin, Texas

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# CORROSION INHIBITION BY ORGANIC AMINES

by

Norman Hackerman and Helmut Kaesche  
Department of Chemistry  
The University of Texas  
Austin 12, Texas

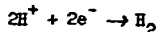
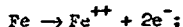
## ABSTRACT

The corrosion of pure iron in 1 N HCl is discussed in terms of the theory of mixed potentials and the same theory applied to the inhibition by organic compounds. Corrosion rates with and without inhibition by aniline, several aniline derivatives, and alkylamines were determined by cathodic polarization measurements as well as by colorimetric analysis of the solution. It is shown that all compounds show a maximum inhibitor efficiency at a concentration of approximately 0.1 mol/l, that with one exception all are cathodic as well as anodic inhibitors, and that in most cases they are predominately anodic inhibitors. An interpretation of the data on cathodic inhibition is suggested on the basis of the assumption of a uniform metal surface and uniform adsorption. The interpretation of anodic inhibition is found to be difficult due to a lack of sufficient experimental data.

. . . . .

There is little question that organic compounds acting as inhibitors of wet corrosion do so by forming an adsorbed layer at the metal-solution interface. As to the details of the mechanism of inhibition there is still considerable difference of opinion. Also, while an extensive literature on inhibition exists, detailed knowledge of the influence of the nature of the inhibitor is still lacking. Therefore it is desirable to accumulate more data on the inhibition efficiency of simple organic compounds with fairly well-known molecular properties. It is for this reason that some experiments with simple aniline derivatives and alkylamines have been carried out and are presented in this paper.

The corrosion of pure iron in air-free 1 N HCl was chosen for the investigation. The over-all corrosion reaction may be split into the anodic and cathodic "partial" reactions:



The electrochemical behavior of the iron specimen as an electrode, including corrosion, is then determined by the kinetics of the partial reactions, these being characterized by their overvoltage curves. This leads to the concept of the superposition of the "partial overvoltage

curves" to the "total current-voltage curve" originally given by Wagner (1) and recently applied to the corroding iron electrode by Uhlig (2), Stern (3), Bonhoeffer (4), and Heusler (5). The following two paragraphs give a short summary of the terms involved. For more detail the papers cited above should be used.

Neglecting the reverse reactions (iron deposition and hydrogen dissolution), the two partial reactions are assumed to have exponential overvoltage curves of the form

$$j_{Fe} = (j_o)_{Fe} \exp. \left[ - \frac{1}{b'_{Fe}} (E_{Fe} - E) \right] \quad (1)$$

$$j_H = (j_o)_H \exp. \left[ \frac{1}{b'_H} (E_H - E) \right] \quad (2)$$

Here  $j_{Fe}$  and  $j_H$  are the apparent anodic and cathodic current densities (based on the geometrical electrode surface  $F$ );  $(j_o)_{Fe}$  and  $(j_o)_H$  are the intercepts of the overvoltage curves with verticals drawn through the equilibrium potentials  $E_{Fe}$  and  $E_H$ ,  $b'_{Fe}$  and  $b'_H$  are the "Tafel" slopes; and  $E$  is the measured electrode potential. Regardless of their actual physical significance  $(j_o)_{Fe}$  and  $(j_o)_H$  are called exchange currents.

If a polarizing current  $j$  is applied from an external circuit, then at any  $j$

$$j = j_{Fe} - j_H \quad (3)$$

This is the equation of the total current-voltage curve which can be measured by external polarization. At  $j = 0$ ,  $E = E_{corr.}$  and

$$|j_{Fe}| = |j_H| = j_{corr.}$$

Here  $j_{corr.}$  is the corrosion rate in terms of an apparent current density, and  $E_{corr.}$  the corrosion potential (open circuit potential). With equations 1, 2, and 3 both the corrosion rate and the corrosion potential are completely determined by the overvoltage properties of the partial reactions. The simultaneous measurement of  $j$ ,  $j_{Fe}$  and  $j_H$  should therefore yield complete knowledge of the electrode behavior in a given surrounding medium. Instead of this procedure, which involves laborious analytical determinations of the amount of dissolved iron, or deposited hydrogen, the electrode may simply be polarized to potential regions where either  $j_{Fe}$  or  $j_H$  becomes very small and therefore  $j \approx j_H$ , or  $j \approx j_{Fe}$ , so that the total current voltage curve is practically identical with one of the partial overvoltage curves. Provided that no change of the rate-determining step of the partial

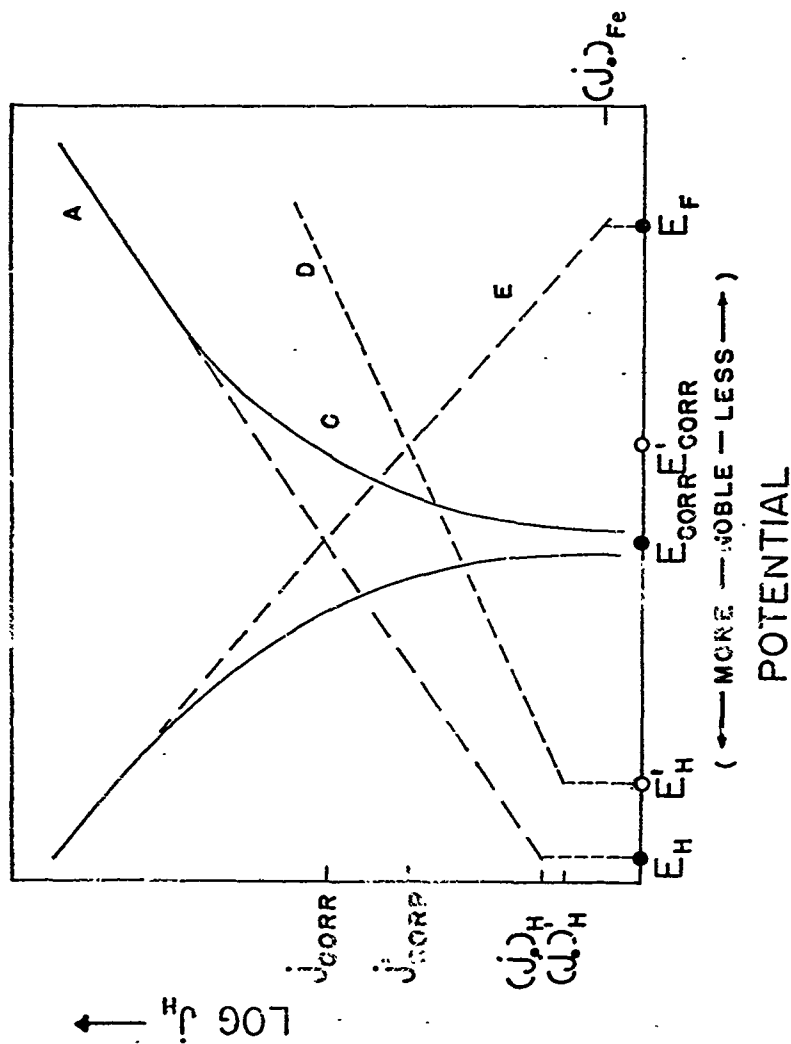
reaction under investigation occurs between this potential region and  $E_{corr.}$ , the partial curve in the vicinity of the latter potential can then be obtained by extrapolation. This simple geometrical operation is illustrated by Fig. 1. Moreover, extrapolation to  $E_{corr.}$  yields the value of  $j_{corr.}$ . Stern (3) has shown that the corrosion rates obtained by extrapolation of the cathodic partial overvoltage curve check well with those determined by analysis of the amount of dissolved iron. The same method is used throughout the present investigation. So far it appears to be difficult to measure the anodic partial curve in the same way, but in the vicinity of  $E_{corr.}$  a part of this curve may be obtained from corresponding values of  $j$  and  $j_H$  by application of equation (3).

The organic inhibitors used for the present investigation do not change the over-all reaction. The lowering of the corrosion rate must therefore be brought about either by a decrease of the distance between the equilibrium potentials  $E_H$  and  $E_{Fe}$ , which can only be brought about by changes of the bulk concentration of the species taking part in the corrosion reaction, or by an increase of the overvoltage of one or both partial reactions. With respect to their action on one or both partial reactions, inhibitors are often classified as being of an anodic, cathodic, or mixed type. The general result of strictly cathodic inhibition is shown in Fig. 1 by the shift of the cathodic partial curve (A) without inhibition to the inhibited curve (D) with inhibition. The inhibition is assumed to decrease the H-equilibrium potential from  $E_H$  to  $E'_H$ , the exchange current from  $(j_0)_H$  to  $(j_0')_H$  and to increase the Tafel slope, while the corrosion rate decreases from  $j_{corr.}$  to  $j'_{corr.}$ . It is clearly seen that whether one, two, or all of the possible changes of the partial cathodic curve occur,  $E_{corr.}$  must always change to a less noble value  $E'_{corr.}$ . Similarly, a reverse change of  $E_{corr.}$  indicates the presence of anodic inhibition. If only the decrease of  $j_{corr.}$  and the shift of  $E_{corr.}$  is observed, only the predominance of anodic or cathodic inhibition can be stated, because at the same time a small effect on the opposite partial reaction may exist, so that the inhibition is actually of the mixed type.

Local cell action between fixed anodic and cathodic areas cannot be affected seriously by the ohmic resistance of the adsorbed layer as long as the above-described polarization method gives the same value for the corrosion rate as the analysis of the solution (or weight loss measurements). The former method is based on the assumption of a virtually uniform electrode potential and must lead to serious errors if IR drops of the order of  $\geq 5$  mV exist along an average current path between local electrodes. Correct polarization values of  $j_{corr.}$  indicate either very short local current paths or low values of the specific resistance of the adsorbed layer. Hoar (6) has suggested that practically the whole electrode surface is capable of acting as a cathodic area, whereas the anodic area should be represented by the sum of all atomic sites undergoing dissolution at any given moment,

Figure 1

Schematic representation of the partial overvoltage curves (dashed curves) and the total current voltage curve (solid curve C) of iron corroding in non-oxidizing acids. (A) - cathodic partial curve; (D) - cathodic partial curve in the presence of a cathodic inhibitor; (E) - anodic partial curve. Other symbols as defined in the text.





where the sites might be; for instance, the ends of incomplete atom rows. With any non-ideal crystal, lattice distortions and included foreign atoms may also give rise to anodic spots. With respect to the relative size of the anodic and cathodic areas and the distribution of anodic spots the condition of the corroding iron surface is then very similar to the condition of the surface of a corroding liquid amalgam, where the cathodic area is identical with the total surface and the anodic area is given by the sum of atoms of the amalgamated metal in the surface of the mercury. Since at any moment predictions can be made that the next iron atom being transferred across the phase boundary should come from the same incomplete atom row or lattice distortion the iron dissolution is still not as truly statistical as the dissolution of an amalgamated metal. Nevertheless, the condition of the corroding amalgam surface should be a better model for the condition of the surface of corroding iron than the frequently-used model of a checkerboard-like pattern of local electrodes. Therefore, the concept of a uniform metal surface undergoing statistical dissolution is used for the discussion of inhibition. It is obvious that this concept, if justified for pure iron, is not immediately applicable to steel surfaces where secondary phases may have considerable influence.

If the electrode surface is uniform, inhibitor adsorption should be general. As has been pointed out by Hoar (7), and Hackerman and Makrides (8), the theory of adsorption of cationic inhibitors on cathodic sites only, for some time widely accepted (as may be seen from papers by Mann (9)) is objectionable even if local cells are operating on the corroding surface, the obvious argument being the uniformity of the electrode potential. The possibility of cation adsorption by means of electrostatic forces is determined by the electric charge of the electrode with respect to the solution, i.e., by the position of the electrocapillary maximum with respect to  $E_{corr.}$ , not by the charge of an electrode with respect to another electrode, as for instance local anodes with respect to local cathodes. Little is known about the electrocapillary maximum of iron and a value of 0.57 V in  $10^{-3}$  N  $H_2SO_4$  measured by Frumkin and co-workers (10) does not indicate that iron corroding in 1 N  $HCl$  ( $E_{corr.} = 0.25$  V) has a positive charge at the corrosion potential. The electrocapillary maximum may be shifted to considerably more noble potentials by chemisorption of  $Cl^-$ , analogous to observations reported by Iofa and co-workers (11) for  $I^-$  and  $Br^-$  at very low concentrations. At present the possibility of strong cation adsorption on corroding iron is therefore undecided. This is important with respect to the theory of chemical rather than physical adsorption, suggested by Hackerman and Makrides (8). According to this concept cationic organic inhibitors are deionized at the metal-solution interface; therefore, in the case of amine-hydrochlorides the adsorbed species should be the free amine. The establishment of a more or less well-defined chemical bond between the inhibitor and the iron should

result in a decrease of the apparent iron activity of the electrode surface (Sackerman (12)). This leaves  $E_{Fe}$  unchanged, but it may greatly decrease the exchange current of the anodic partial reaction.

#### MATERIAL AND APPARATUS

Iron electrodes were cut out of 99.99% Armco iron sheets, 1 mm in thickness, in the shape of little flags of about 4 to 5 sq.cm. geometric surface area. The handle of these flags was soldered to a copper wire and sealed into a glass holder with polyethylene. Before immersion, the electrodes were abraded with No. 1 through 4/0 emery paper, and rinsed with benzene, acetone, and water.

1 N HCl solutions were prepared from C.P. concentrated HCl and double-distilled water. No change of the corrosion rate was observed when gaseous HCl distilled into water was used instead.

Except for methylamine- and ethylamine-hydrochloride, which were used without further purification of the high-grade compound, all inhibitors were redistilled one to three times under reduced pressure, until a colorless product of constant boiling point was obtained. The inhibitors were then dissolved in the appropriate amount of concentrated HCl to give a 1 N HCl solution of the hydrochloride. No inhibitor solution was used later than three days after preparation.

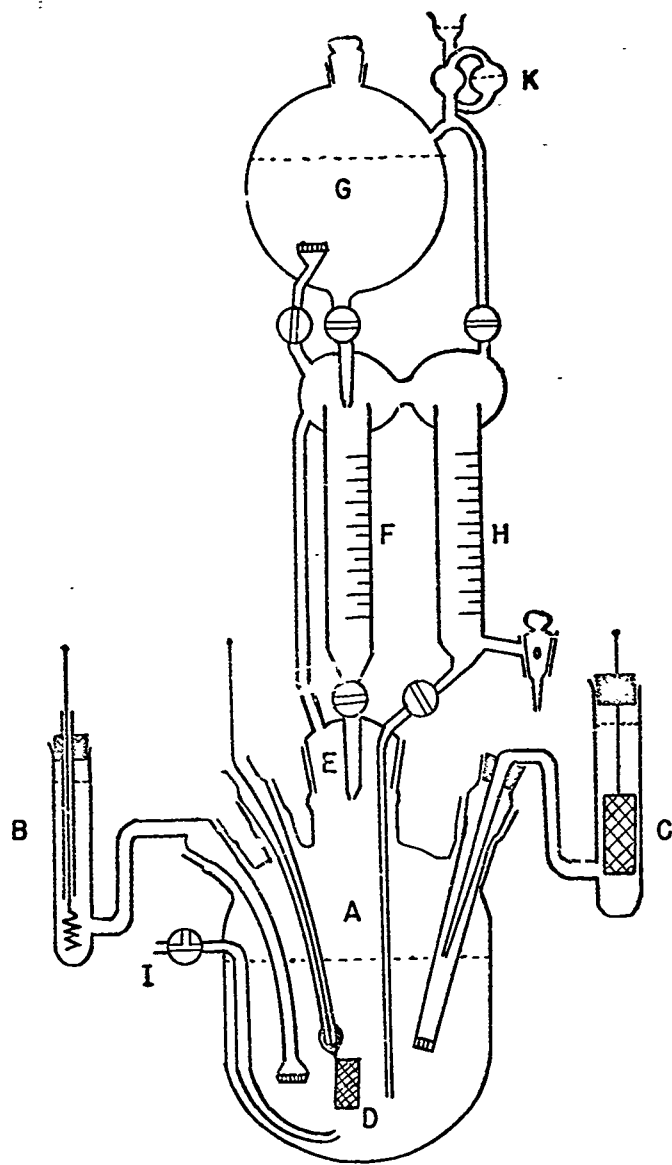
Electrolytic hydrogen was passed through pyrogallol acid in alkaline solution, sodium plumbite in alkaline solution, concentrated  $H_2SO_4$ , a trap cooled with liquid nitrogen, and finally a 50-cm. column of 1 N HCl before being bubbled through the test solution. Omitting this procedure resulted in a marked decrease of the corrosion rate.

The apparatus used throughout the experiments is shown in Fig. 2. All parts were made of Pyrex, with stoppers and stopcocks very lightly greased with silicone grease. The test vessel A, the Ag/AgCl-electrode B, and the Pt-electrode C, were filled with 1 N HCl up to the dotted lines. Three iron electrodes, D, of which only one is shown, are used at the same time.

The outlet of burette F was sealed into the ground joint E and on top of F a flask G served as a reservoir for inhibitor solutions. A second burette H was also sealed into E and was extended via capillary tubing into the test solution. Hydrogen entered the apparatus at I and left it at K, thus keeping all parts air-free and also slightly agitating the solution. If hydrogen was bubbled through the solution more vigorously the corrosion potential and the corrosion rate did not change by more than 1 mV and 1  $\mu A/sq.cm.$  The test vessel was placed in a thermostat kept at  $30 \pm 0.5^\circ C$ . The volume of the test solution in A was 500 cc., all pH changes due to the corrosion reaction were negligible.

Figure 2

Apparatus used for the measurement of overvoltage  
properties and corrosion rates.



The potential difference between the Fe-electrode and the Ag/AgCl-reference electrode was measured with a student-type potentiometer within  $\pm 1$  mV. In order to be able to make quick readings during polarization measurements, an oscilloscope was used as zero indicator. Polarizing currents were applied between the Fe- and the Pt-electrode, using a 220 V. dry battery in series with a resistance box and a milliammeter. Current readings were taken with a precision of  $\pm 5 \mu\text{A}$  at currents between 1 and 3 mA and  $\pm 2 \mu\text{A}$  at currents less than 1 mA. The resistance of the electrode system was small compared with the external ohmic resistance, the polarizing currents were therefore constant during the polarization time.

#### PROCEDURE AND RESULTS

After the electrodes had been immersed in air- and inhibitor-free 1 N HCl a period of 3 to 5 hours was required for both  $E_{\text{corr.}}$  and  $j_{\text{corr.}}$  (\*) to become constant. After 5 hours,  $E_{\text{corr.}}$  and  $j_{\text{corr.}}$

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\*0 designates uninhibited properties.

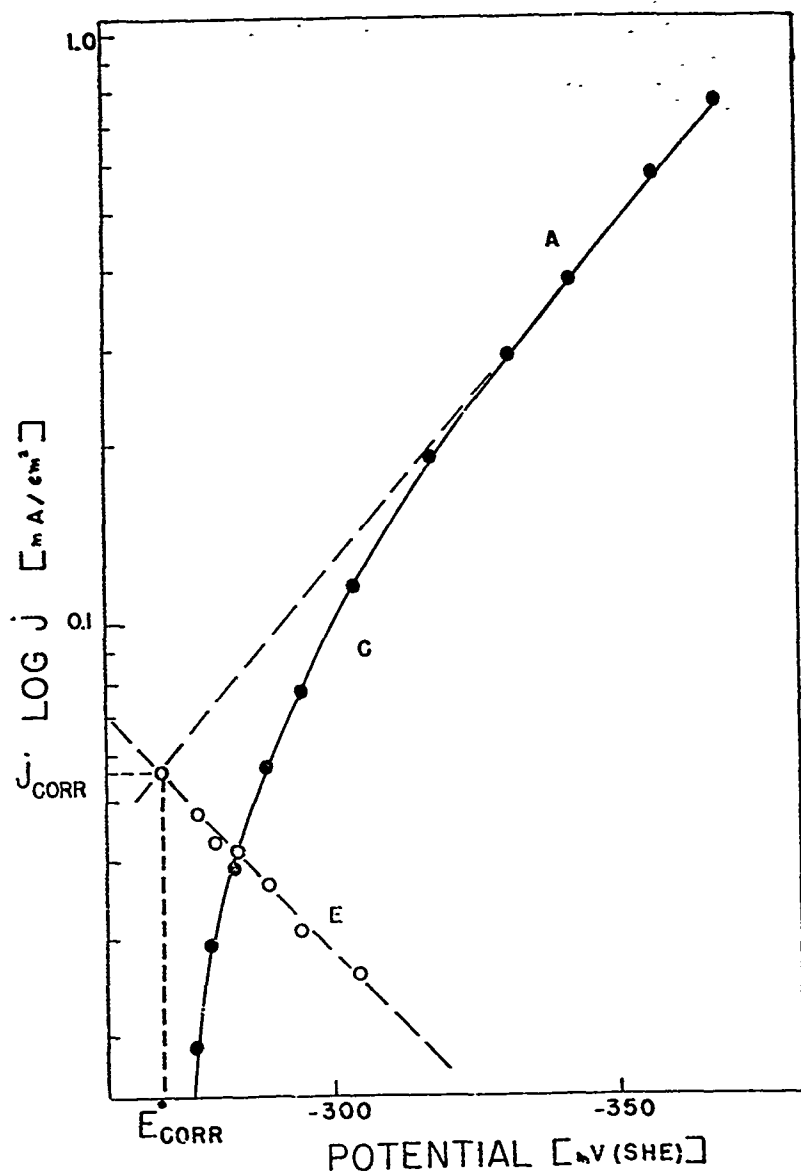
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were constant in most cases except for random changes of  $\pm 1$  mV/hour and  $\pm 3 \mu\text{A}/\text{sq.cm.}/\text{hour}$  respectively. The polarization behavior of all electrodes was checked at one-hour intervals throughout the immersion time, but only the readings taken between 5 and 7 hours after immersion were used for the final determination of the overvoltage properties. A considerable number of runs had to be discarded because of (a) corrosion rates more than  $5 \mu\text{A}/\text{sq.cm.}$  lower or higher than the average of all measurements, (b) non-constant values of  $E_{\text{corr.}}$  and  $j_{\text{corr.}}$  after 5 hours, (c) potential drifts during polarization. Any drift greater than 1 mV/10 sec. observed later than 10 sec. after switching on the polarizing current was regarded as abnormal and attributed to contamination of the acid. In all cases of erratic behavior the electrodes were freshly sealed to the glass holder, freshly abraded and rinsed, and the test solution replaced by freshly prepared solution. No inhibition experiment was carried out until a given set of electrodes exhibited "normal" behavior, with  $E_{\text{corr.}}$   $-260 \pm 10$  mV (vs. S.H.E.),  $j_{\text{corr.}}$   $50 \pm 5 \mu\text{A}/\text{sq.cm.}$  and non-drifting potentials during cathodic polarization.

A typical example of a single polarization measurement with an uninhibited specimen is shown in Fig. 3.  $E_{\text{corr.}}$  was measured immediately before the first polarization (immediately afterwards  $E_{\text{corr.}}$  is usually 1 to 2 mV more noble than before, but the original value is reestablished within a minute). Cathodic currents of various strength were applied at 30-second intervals and the polarized potentials  $E$  measured with the potentiometer (solid circles) 5 to 10 seconds after switching on the current. The total current-voltage curve obtained as

Figure 3

Total current-voltage curve and partial overvoltage curve determined by cathodic polarization of an iron electrode in 1 N HCl without inhibition. Symbols as given in the caption of Figure 1; other symbols as defined in text.



as  $E$  vs.  $\log j$  (solid curve) was always found to have a linear section in the current range  $0.2 \leq j \leq 0.7$  mA/sq.cm. which could easily be extrapolated to  $E^0_{\text{corr.}}$  (dashed curve). From this curve, presumably the cathodic partial overvoltage curve,  $j^0_{\text{corr.}}$  and  $b^0_H (=b^0_{\text{Fe}}/2.303)$  were determined graphically. In a few cases the non-linear part of the logarithmic total current voltage curve was also measured to obtain examples of the anodic partial overvoltage curve by application of equation 3 (open circles and broken line). Thus the slope  $b^0_{\text{Fe}}$  of the anodic curve was found to be of the order of  $0.075 \pm 0.01$  volt/ $\log j$  which may be compared with Stern's (13) value 0.068, determined by the same method in NaCl + HCl solution of pH 1.5 at 25°C. The exchange current  $(j_0)_{\text{Fe}}$  was calculated to be of the order of 0.04 to 0.1  $\mu\text{A/sq.cm.}$  which again checks fairly well with Stern's value 0.04  $\mu\text{A/sq.cm.}$  measured under the quoted conditions noted. However, the error limit of any single determination of  $(j_0)_{\text{Fe}}$  is  $\pm 0.02$  and any attempt to calculate the change of the exchange current due to weak inhibitor action is therefore useless.

In order to avoid erroneous results caused by slow drifts of the electrode properties during immersion over several days, all electrodes were again abraded and rinsed before addition of inhibitors to the solution. Also, usually after two complete series of experiments for one inhibitor new electrodes were prepared. Otherwise the measurements in inhibited solutions were carried out exactly as were those without inhibitors. In addition to  $b_H$  and  $j_{\text{corr.}}$  a property  $j'$ , the cathodic partial current of the inhibited electrode at  $E^0_{\text{corr.}}$  was determined. Especially after addition of the more effective inhibitors a slow drift of the potential of externally-polarized electrodes to less noble potentials, presumably caused by changes of the adsorption concentration of the inhibitor, could not be eliminated. Using the potentials obtained 5 to 10 sec. after switching on the polarizing current, allowing 1 minute intervals between two consecutive polarizations, and also limiting the polarizing currents to 0.5 mA/sq.cm. in cases where the logarithmic total current-voltage curve became linear at 0.15 - 0.17 mA/sq.cm. because of the lowered  $j_{\text{corr.}}$ , correct values of  $j_{\text{corr.}}$  were nevertheless obtained. This was shown by independent analytical measurements. For this control, polarization measurements were carried out between 2 and 8 hours after immersion in separate runs at one-hour intervals, and samples of the solution were taken at the same time. The  $\text{Fe}^{++}$  concentration of the samples was then determined colorimetrically, using o-phenanthroline as complexing agent. The average values of the corrosion rate obtained by polarization checked well with the corrosion rate determined by analysis (Table I).



Table I

Comparison of the average total corrosion rate of 3 electrodes  
obtained by cathodic polarization ( $i_1$ ) and by colorimetric  
analysis ( $i_2$ ) - C = inhibitor concentration

Inhibitor	C (mol/l)	$i_1$ ( $\mu$ A)	$i_2$ ( $\mu$ A)
-	0	$820 \pm 20$	$840 \pm 50$
N-Methylaniline	0.06	$720 \pm 20$	$700 \pm 20$
N-Ethylaniline	0.05	$490 \pm 10$	$490 \pm 10$
N-Propylaniline	0.12	$355 \pm 10$	$350 \pm 20$

Usually 3 to 4 runs at inhibitor concentrations between 0.05 and 0.2 mol/l were carried out. For each inhibitor concentration final values of  $j_{\text{corr.}}$ ,  $j'$ ,  $b_p$ , and  $E_{\text{corr.}}$  were obtained by obtaining the algebraic mean of six single measurements, two per electrode. A typical example of the resulting curves of the electrode properties as a function of concentration is shown in Fig. 4 for m-toluidine. At  $C \geq 0.08$  to 0.1 mol/l, all inhibitors showed a maximum effect on the electrode properties independent of further increase of concentration up to 0.2 mol/l, the highest concentration investigated. As no attempt was made to measure fully the changes of the electrode properties at concentrations  $0 \leq C \leq 0.1$ , Table II lists only the electrode properties at maximum inhibitor effect obtained graphically from plots of the experimental values against concentration. With propylamine as inhibitor the slope  $b_{Fe}^0$  of the anodic partial overvoltage curve was determined at maximum inhibitor effect and found to be of the order of  $0.030 \pm 0.01$  volt/log i.

The error limits given in the tables are caused by differences in the behavior of different electrodes. Compared with these differences the limited precision of the measurements has little significance. This includes the error introduced by the resistance between the tip of the reference electrode and the iron electrodes (approximately 2 cm.). It does not include the error limit of the colorimetrically-determined values of  $j_{\text{corr.}}$ .

Figure 4

The variation of the corrosion potential  $E_{\text{corr}}$  and the corrosion rate  $j_{\text{corr}}$  of a set of three iron electrodes as function of the concentration of m-toluidine hydrochloride of the solution.

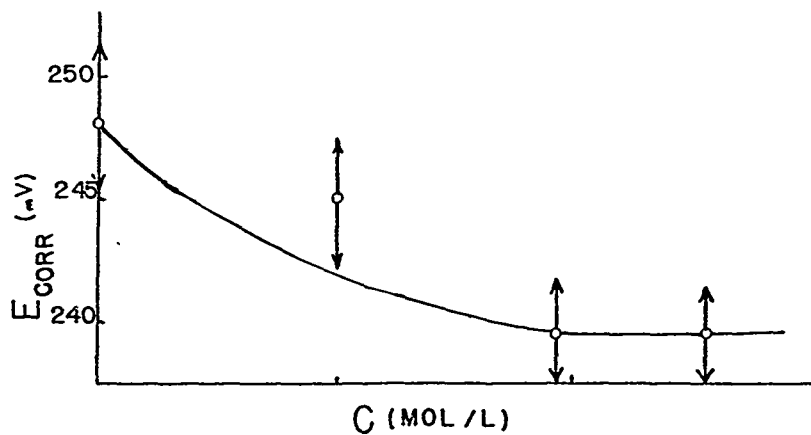
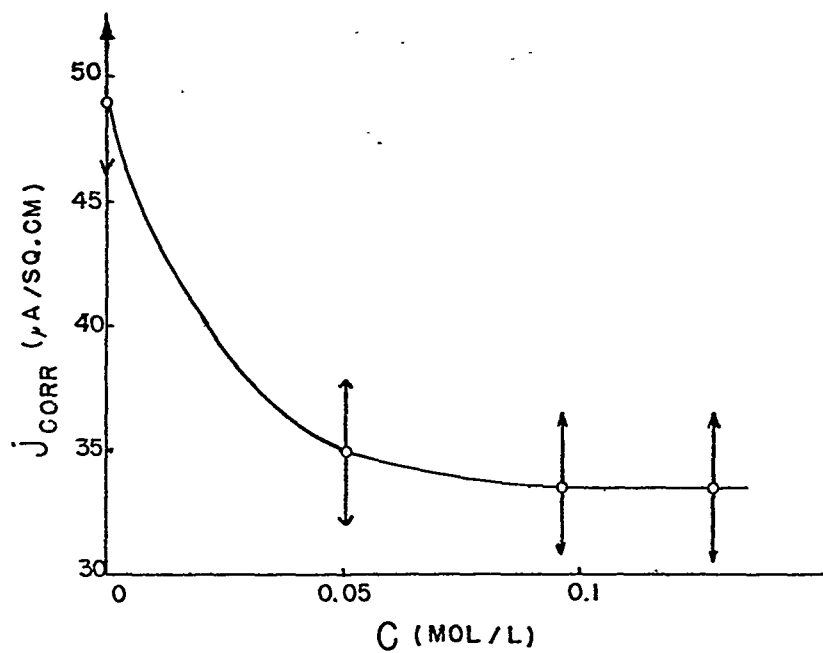


Table II

Average value of the corrosion potential  $E_{\text{corr}}$ , the corrosion rate  $j_{\text{corr}}$ , and the cathodic Tafel slope  $b_H$  of three electrodes with no inhibition (o) and at maximum inhibition (m), also the cathodic current at maximum inhibition at  $E_{\text{corr}}^o$ . The error limits listed do not apply for  $b_H^m$  in the case of aniline and N-Propylaniline where it was  $\pm 0.004$ .

Inhibitor		$E_{\text{corr}}^o$	$b_H^o$	$j_{\text{corr}}^o$	$j'$
		$E_{\text{corr}}^m$ (mV)	$b_H^m$ (v/log i)	$j_{\text{corr}}^m$ ( $\mu\text{A}/\text{sq.cm.}$ )	
Aniline	o	-249	0.091	47	40
	m	-237	0.090	30	
M-Toluidine	o	-248	0.092	48	42
	m	-239	0.093	33	
o-Toluidine	o	-257	0.086	51	44
	m	-240	0.091	29	
N-Methylaniline	o	-249	0.092	51	46
	m	-241	0.089	38	
N-Ethylaniline	o	-259	0.088	53	46
	m	-260	0.094	37	
N-n-Propylaniline	o	-267	0.089	49	38
	m	-258	0.095	32	
N-Dimethylaniline	o	-249	0.085	53	47
	m	-231	0.085	31	
N-Diethylaniline	o	-268	0.083	54	34
	m	-255	0.093	25	
N-Di-n-propylaniline	o	-266	0.084	53	29
	m	-252	0.093	24	
Methylamine	o	-265	0.086	52	43
	m	-268	0.086	45	
Ethylamine	o	-268	0.091	54	42
	m	-268	0.091	42	
Propylamine	o	-269	0.085	55	44
	m	-267	0.091	42	
Error limit		$\pm 2$	$\pm 0.002-3$	$\pm 2$	$\pm 3$

## DISCUSSION

### (a) Inhibition of the Cathodic Partial Reaction.

Table II shows that with all inhibitors  $j'$  is lower than  $j^{\circ}_{\text{corr}}$ , and in many cases  $b^m_H$  is larger than  $b^0_H$ . Therefore, all inhibitors investigated exhibit cathodic inhibitor action. To obtain a quantitative measure of this action it is recalled that with  $b_H = \text{constant}$  the quotient  $j'/j^{\circ}_{\text{corr}}$  must equal the quotient  $(j_0)_H^m/(j_0)_H^0$  and therefore be a measure of the decrease of the cathodic exchange current. Even for small values of  $\Delta b$  ( $=b_H^m - b_H^0$ ) the same relationship holds to a first approximation and is therefore calculated for each inhibitor. Following common usage in inhibitor research, instead of  $j'/j^{\circ}_{\text{corr}}$  itself, Table III lists the quantity  $(1 - j'/j^{\circ}_{\text{corr}}) \cdot 100\% = I_c$ . Neglecting the influence of  $\Delta b_H$  this quantity is called the "cathodic inhibitor efficiency" (not identical with the inhibitor efficiency which would be observed with a given  $I_c$  in the absence of all anodic inhibition). The values of  $\Delta b_H$  and the "total inhibitor efficiency"  $I_T = (1 - j^m_{\text{corr}}/j^0_{\text{corr}}) \cdot 100\%$  are also tabulated. It is seen that  $I_c$  is practically constant for the alkylamines and the group formed by aniline and the toluidines. With increasing chain length of the substituent of N-alkylanilines  $I$  increases, this increase being more pronounced in the series of N-dialkylanilines than in the series of N-monoalkylanilines.

Remembering that all numbers are limiting values for maximum inhibition and therefore probably maximum adsorption, it can be expected that the adsorbed molecules are oriented nearly perpendicularly to the surface. If this is true, then the observed tendencies of the change of  $I_c$  strongly suggests an effect of the projected area per molecule. For perpendicularly oriented molecules the projected area of straight chain alkylamines is independent of the chain length and equals the projected area of the amine group. On the other hand, perpendicular adsorption of a N-substituted aniline means that all substituents form an angle smaller than  $90^\circ$  with the metal surface. An increase of chain length consequently increases the projected area. Also, with N-dialkylanilines a larger increase of the projected area is to be expected since two methyl groups are added instead of one in the case of N-monoalkylanilines. While no quantitative interpretation is possible it is clear that for alkylamines, and N-alkylamines changes of  $I_c$  parallel changes of the projected area within each group. As  $I_c$  is constant for aniline and the toluidines it has to be concluded that only substitution for H on the nitrogen is effective, that is, close to the surface of the underlying metal. It is also possible, that a smaller effect would be observed on increasing the chain length of the substituent on the benzene ring.

Table III

The total cathodic and anodic inhibitor efficiency calculated for each inhibitor from  $j_{corr}^c$ ,  $j'$  and  $j''$ , respectively, and  $j_{corr}^o$ , as found in uninhibited solution with the same set of electrodes, also  $\Delta b_H = b_H^m - b_H^c$  calculated in the same way.

Inhibitor	$I_T$ (%)	$I_c$ (%)	$\Delta b_H$ (v/log i)	$I_a$ (%)
Aniline	36	15	-0.001	55
m-Toluidine	31	13	+0.001	46
o-Toluidine	43	14	+0.005	65
N-Methylaniline	25	10	-0.003	41
N-Ethylaniline	30	13	+0.006	47
N-n-Propylaniline	36	26	+0.006	53
N-Dimethylaniline	41	11	0.000	66
N-Diethylaniline	54	37	+0.010	68
N-Di-n-propylaniline	57	40	+0.008	71
Methylamine	13	18	0.000	0
Ethylamine	17	20	+0.002	20
Propylamine	23	20	+0.006	29
Error limit	4	4	0.003-4	4

If all types of aniline derivatives investigated have the same maximum number of moles adsorbed per sq. cm. of the metal, then the total projected area should increase in the series aniline, N-methylaniline, N-dimethylaniline, and  $I_0$  should also increase. Actually  $I_0$  is greater for aniline than for both N-methyl- and N-dimethylaniline, and practically constant for the latter two compounds. Experimental data for the maximum adsorbed amount are not available but it is reasonable to predict a decrease with increasing branching of the substituents due to steric hindrance. Therefore it is likely that, while the projected area per molecule increases, the total projected area decreases from aniline to N-methylaniline because of a decrease of the number of adsorbed moles, and the decrease of  $I_0$  is therefore not contradictory. The decrease of  $(j_0)_H$  is usually ascribed to a decrease of the true surface area available for hydrogen deposition (6,7,9). With respect to this the observed changes of  $b_H$ , neglected in the discussion just above, is of importance. In principle, changes of  $b_H$  can indeed be caused by mere changes of the true surface area available. This follows not only for the case of competing adsorption of inhibitor and H-atoms but also because of competing parallel reaction paths for H-deposition (e.g., slow discharge followed by Tafel recombination, and electrochemical mechanism) depending to a different degree on the H-concentration of the surface. However, this requires very special assumptions not justified by experimental evidence. Less elaborate, and therefore for the time being preferable, is the assumption that both partial reactions are controlled by an energy barrier at the phase boundary which requires a slow discharge mechanism for the cathodic partial reaction. According to the theory of H-overvoltage  $b_H$  should then be of the form  $2.303 RT/\alpha zF$ , where R is the gas constant, T the absolute temperature,  $\alpha$  a factor between 0 and 1, z the electron number, and F the Faraday. For iron in different inhibitor-free solutions values of  $b_H$  between 0.08 and 0.15 volt/log i have been observed by different authors (3,5,13,14) indicating values of  $\alpha$  ranging from 0.7 to 0.4. The average value of  $b_H$  found during the present investigation is  $0.088 \pm 0.004$ ,  $\alpha$  therefore is 0.66. The theory of slow discharge predicts  $\alpha = 0.5$  for the case that exactly half of the overvoltage is used to lower the activation energy of the forward reaction, the other half being used to increase the activation energy of the reverse reaction. However, this ideal symmetry need not be followed in every case, and with a different  $\alpha$ , slow discharge (or the electrochemical mechanism) may still be rate-determining. If this is accepted for the cathodic partial reaction it follows that an increase of  $b_H$  indicates a decrease of  $\alpha$  and therefore a decrease in the fraction of the cathodic overvoltage used to lower the activation energy of the  $H^+$  transfer across the phase boundary. This requires a distortion of the potential distribution in the phase boundary. It is then reasonable to assume that the cause of this distortion is the establishment of an additional energy barrier due to inhibitor adsorption. Consequently the inhibitor layer is treated as a uniform film which leaves the available surface unchanged but increases the activation energy of  $H^+$  transfer, thus decreasing the probability of this transfer. While the distortion of



the potential distribution is responsible for the change of  $b_{Fe}$ , the lowering of the transfer probability is responsible for the decrease of  $(j_0)_{Fe}$ . The observed influence of the total projected area is then not an influence of the increasing degree of surface blanketing, but of the increasing density of the uniform inhibitor layer, where the increase in density is expected to cause a proportional increase in the activation energy. In view of the considerable error limit of the  $\Delta b_{Fe}$  values no similar interpretation of  $b_{Fe}$  as a function of the molecular structure of the inhibitor can be attempted.

#### (b) Inhibition of the Anodic Partial Reaction.

Except for the single pair of data of  $b_{Fe}$  before and after addition of propylamine as inhibitor no other information on anodic inhibition has been obtained except the shift of  $E_{Fe}$ . Assuming  $b_{Fe} = \text{constant} = 0.075$  for inhibited and uninhibited electrodes the anodic partial current  $j^a$  of the inhibited electrode at  $E^0_{corr.}$  can be obtained from  $I_{corr.}$  and  $I_c$  and a quantity  $(1 - j^a/j^0_{corr.}) \cdot 100\% = I_a$  can be calculated which is comparable to  $I_c$ . This has been done graphically and the resulting values of  $I_a$ , listed in Table III is used for the discussion of anodic inhibition instead of the shift of  $E^0_{corr.}$ . In view of the arbitrary assumption  $b_{Fe} = \text{constant}$  the same error limit has to be attributed to the  $I_a$  values as to those of  $I_c$ . Within this limit  $I_a$ , if not a measure of the decrease of  $(j_0)_{Fe}$ , is at any rate a measure of the anodic inhibition and therefore justly called the "anodic inhibitor efficiency". Inspection of Table III shows that with the exception of methylamine all inhibitors investigated exhibit anodic as well as cathodic inhibition and are therefore inhibitors of the mixed type. Furthermore it is also seen that all aniline derivatives are of a predominantly anodic type.

$I_a$  is zero for methylamine and increases rapidly with increasing chain length of alkylamines. It has already been argued that the total projected area for alkylamines is constant with respect to the cathodic partial reaction. Within the concept of general adsorption and uniform electrode surface, the same must be true for the anodic partial reaction. An explanation of the increase of  $I_a$  in spite of constant total projected area, is offered by the theory of chemisorption. It has been pointed out by Hackerman and Makrides (8) that chemisorption of amines should increase with electron donor properties and that lacking other data the basicity of the free amine should be considered representative of these properties. As the basicity of the alkylamines used here is practically constant (15), this suggestion gives no clue as to the variation of chemisorption of these compounds. Therefore, it can only tentatively be assumed that the contribution of chemisorption to the total adsorption may increase with increasing chain length, while the total adsorbed amount, and therefore the total projected area, remains constant because of the existence of a saturated monolayer of adsorbed amines. As has been mentioned before, this can be expected

to result in a decrease of the apparent iron activity of the electrode surface. If slow charge transfer across the interface is rate-determining for the anodic partial reaction, the anodic exchange current  $(j_0)_{Fe}$  may then be treated as the product of the true surface area  $F$  (which is constant if the concept of uniform adsorption is correct), a transfer probability  $P$  (the probability of the penetration of the activation barrier across the double layer by  $Fe^{++}$ ) and the iron surface activity  $A$ . The predominance of anodic inhibition can then be interpreted as being due to the lowering of  $A$  by chemisorption, where the lowering of  $P$  by inhibitor adsorption could be roughly the same as that for the cathodic inhibition.

Aniline derivatives are much less basic than straight chain alkylamines, but they are nonetheless the better anodic inhibitors. The N-alkylanilines show a comparatively small increase of  $I_c$  with increasing chain length of the aliphatic substituent but it is doubtful whether this can be attributed to the basicity. Basicity constants of aniline derivatives (15) in dilute solutions show that the basicity does not increase regularly with chain length of aliphatic substituents. The difference in basicity of different compounds is usually small, so that no predictions as to the basicity in concentrated solutions are possible. Both the total amount and the differences of anodic inhibition observed with aniline derivatives are therefore difficult to explain. Considering that within each group of N-alkylanilines the changes of  $I_a$  parallel the changes of  $I_c$  it may tentatively be assumed that this indicates an influence of the energy barrier similar to that of the cathodic partial reaction. Whether the large total value of  $I_a$  is caused by additional strong chemisorption of the aniline derivatives cannot be decided here.

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